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# MINERALS FROM MACEDONIA
## XII. THE DEPENDENCE OF QUARTZ AND OPAL COLOR ON TRACE ELEMENT COMPOSITION – AAS, FT IR AND MICRO-RAMAN SPECTROSCOPY STUDY

**Petre Makreski[1], Gligor Jovanovski[1], Trajče Stafilov[1], Blažo Boev[2]**

[1]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University, P.O Box 162, MK-1001 Skopje, Republic of Macedonia*
[2]*Faculty of Mining and Geology, Ss. Cyril and Methodius University, MK-2000 Štip, Republic of Macedonia*
petremak@iunona.pmf.ukim.edu.mk

The dependence of the color of quartz and opal natural minerals, collected from different localities in the Republic of Macedonia (Alinci, Belutče, Budinarci, Mariovo, Sasa, Saždevo, Čanište, Češinovo, Zletovo) on their element composition is studied using Fourier transform infrared spectroscopy (FT IR), micro-Raman spectroscopy and atomic absorption spectrometry (AAS). In order to determine the content of different trace elements (Al, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn), 15 quartz and 2 opal mineral samples, using flame atomic absorption spectrometry (FAAS) and Zeeman electrothermal atomic absorption spectrometry (ETAAS) are studied. To avoid matrix interferences, the method for elimination of silicium is proposed. Optimal instrumental parameters for ETAAS determination (temperature and time for drying, pyrolysis and atomizing) are established by extensive testing for each investigated element. It is found that the milky white color of quartz minerals is due to the presence of traces of Ca, the appearance of black color is the result of the existence of Pb, Mn and Al impurities, and the occurrence of Fe and Cr introduce appearance of red and green color, respectively.

Preliminary identification of the minerals is based on the comparison of our results, obtained by using the infrared and Raman vibrational spectroscopy, with the corresponding literature data for the analogous mineral species originating all over the world.

An overview of the basic morphological and physico-chemical characteristics of the quartz and opal minerals and the geology of the localities is given. The colored pictures of the studied quartz and opal minerals are presented as well.

**Key words:** quartz; opal; color; minerals; Macedonia; FT-IR spectroscopy; Raman spectroscopy; atomic absorption spectrometry

## INTRODUCTION

Minerals are natural occurring inorganic substances with a relatively constant chemical composition and fairly defined physical properties. Minerals obtained during the long geological period of their formation are not absolutely pure without any contamination. It means that most minerals contain extraneous substances that change some of their characteristics. There are a number of elements that are quite easily interchangeable, influencing one mineral to grade into another. Also there are many cases where some inclusions into mineral crystals are introduced. Therefore, there are important reasons to analyze trace elements in different minerals: i) to determine the purity of minerals; ii) to get information about the geology of mines and mine localities; iii) to detect very rare and important elements etc.

The pure quartz is colorless, but the presence of impurities may cause a whole range of colors [1]. Several studies have been conducted linking the black [2], brown [1], blue [1, 3–6], green [1, 2, 7–12], violet [9], pink [2, 3, 10, 13–16], yellow

and orange [2, 17] and red [1, 2, 18] color with its trace element composition. Some quartz varieties are not caused from the presence of trace elements, but from the structural differences. For example, it is found that milky quartz appears due to numerous bubbles of gas and liquid in the crystal [1].

Opal or amorphous silica, is commonly colorless. One of the most striking qualities of the less-common colored gem variety is its ability to reflect and refract specific wavelengths of light. The differences between the two forms are not related to chemical compositional differences between the two materials [19]. Color, particularly in red hues, is often found in opals both with and without diffraction colors [2]. These hues are commonly encountered in opal and the red colors are associated with $Fe^{3+}$ oxidation state of iron. Opals from some localities are colored blue due to the presence of copper minerals [2].

In this study various trace elements (Al, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) in 15 quartz and 2 opal samples are analyzed by flame atomic absorption spectrometry (FAAS) and Zeeman electrothermal atomic absorption spectrometry (ETAAS). Preliminary identification of the studied minerals is performed using vibrational (FT IR and Raman) spectroscopy.

The infrared [20–25] and Raman spectrum of $\alpha$-quartz [26–30] have been extensively studied for many years, mostly, because of its piezoelectric characteristics, lack of inversion center (manifested by the appearance of the polar modes in both the infrared and the Raman spectrum) and temperature dependence of the several modes across the $\alpha$-$\beta$ phase transitions. Despite the large number of experimental and theoretical studies of the assignment of the bands, its vibrational spectrum is still not well-understood [26].

Basic morphological and physico-chemical characteristics of the minerals and the geology of the localities are given as well as the colored pictures of the studied quartz and opal minerals.

## EXPERIMENTAL

### *Samples*

The studied quartz samples collected from different localities in the Republic of Macedonia are included: Budinarci (4 samples), Mariovo (4), Alinci (2), Čanište (1), Belutče (1), Sasa (1), Zletovo (1), Saždevo (1). Two opal samples from Češinovo locality are also studied.

The crystals of the investigated minerals are carefully picked up under a microscope from the ore samples and then powdered.

### *Instrumentation*

The mid IR spectra of the studied samples are recorded on Perkin-Elmer FT IR system 2000 interferometer using the KBr pellet method for the sample preparation.

The Jobin-Yvon LabRam Infinity spectrometer with microscope ($f$ x 20) and with 532 nm laser line of a Nd-YAG frequency-double laser is employed for recording the presented Raman spectra. The measurements are carried out at the room temperature and spectral data analyzed with the GRAMS/32 software package.

A Varian SpectrAA 640Z Zeeman electrothermal atomic absorption spectrometer with a Varian PSD-100 Autosampler is used for determination of the content of trace elements Cd, Co, Cr, Cu, Ni and Pb. The FAAS measurements of analytes are carried out by Thermo Elemental Solaar S4. Thermo Solaar S4 also served for flame atomic emission spectrometry (FAES) of sodium and potassium.

### *Dissolution of mineral samples*

The powdered quartz and opal samples (0.1–0.2 g) are put into platinum crucibles and 5 ml conc. $HNO_3$, 2 ml HCl, 1 ml $H_2O_2$ and 2 ml of HF are added. Crucibles are heated on hot plate and the solution evaporated to near dryness. After that 1–2 ml HF are added few times until precipitate of $SiO_2$ is eliminated as $SiF_4$ vapors. After cooling down to the room temperature, 2 ml conc. HCl and 5 ml redistilled water are added, the solution transferred in 50 ml volumetric flasks and filled up with redistilled water.

### *Gravimetric determination of $SiO_2$*

0.5 g of powdered sample is put in a glass beaker, 15 ml redistilled water, 20 ml conc. HCl are added and the solution evaporated to near dryness. The residue is dissolved with 10 ml 1 % gela-

tin and $SiO_2$ precipitated and coagulated. Precipitate is filtered and washed with HCl solution (5:95). Filter paper and residue are transferred into a platinum crucible and heated on 1000 °C for 10 min. Crucible is weighed and the content of $SiO_2$ calculated.

## MINERAL ASSOCIATIONS OF THE STUDIED QUARTZ AND OPAL

A brief overview of the basic morphological and physico-chemical characteristics of the quartz and opal minerals is given below. The localities with the particular aspect on their geology are described and are placed in the map of the Republic of Macedonia (Fig. 1).

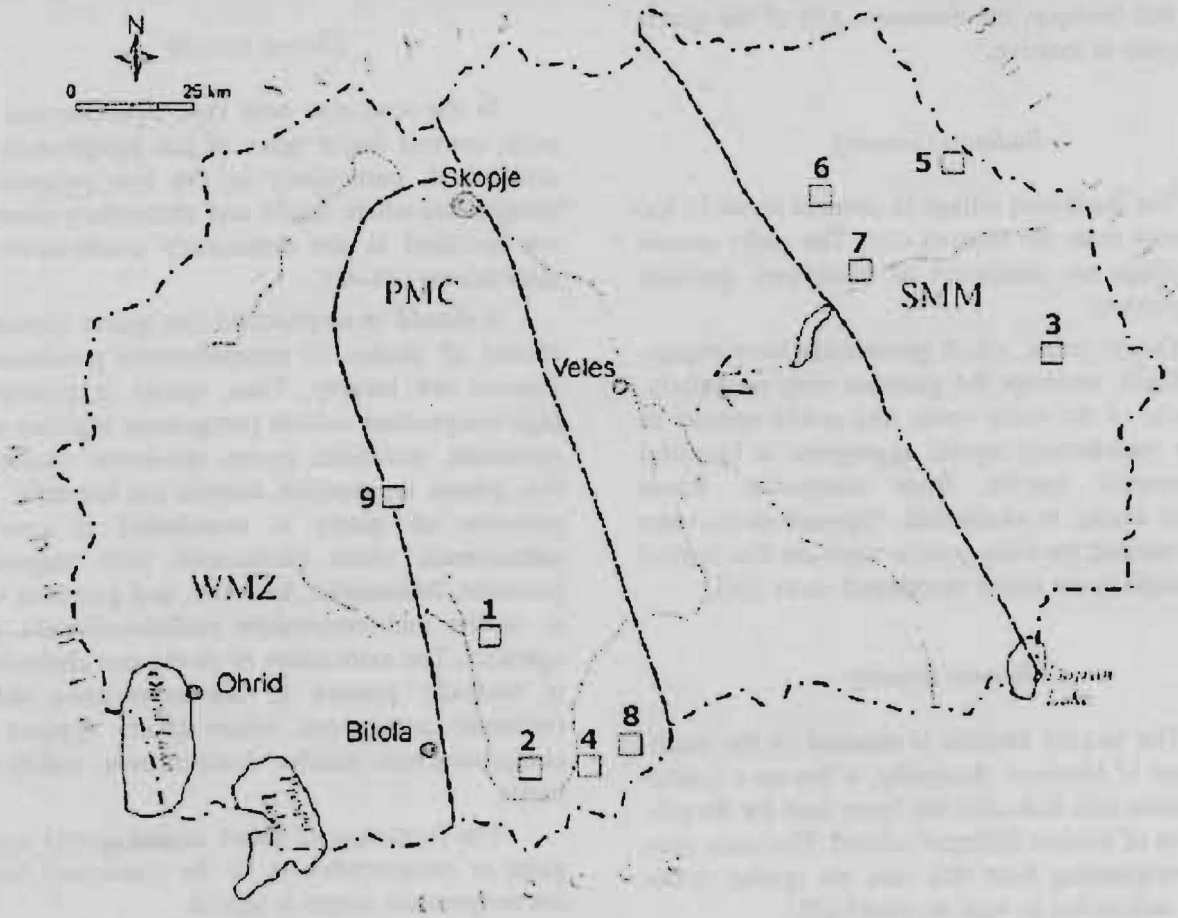



**Fig. 1.** The localities of the studied quartz and opal samples in the Republic of Macedonia:
1) Alinci, 2) Čanište, 3) Budinarci, 4) Belutčc, 5) Sasa, 6) Zletovo, 7) Češinovo, 8) Mariovo, 9) Saždevo

### *Alinci locality*

The geology of Alinci locality is characterized with alkali syenites, amphibolites, gneisses, and muscovite schists and marbles [31].

Quartz with different size crystals emerges in aplite and pegmatite veins, which are basically built up of quartz and microcline. According to this type of origin, the appearance of incorporation between the quartz and microcline occurs. Since arfvedsonite is very common for this locality [32], the quartz crystals are fulfilled with needles of this mineral. It means that, in the process of their formation, the development of quartz comes after the arfvedsonite formation.

### *Čanište locality*

On the western edge of Selečka Planina the locality Čanište lies. This deposit is remarkable because of the large number of scattered minerals which originate from the pegmatite (in the garnets) and gneiss series [33].

The Čanište pegmatite body is lens-formed, but deep in the ground it becomes thinner and adopts vein structure. It is mainly made from feldspars (amazonite), muscovite, garnet, biotite and quartz. The latter appears in the inner part of the body whereas the feldspars surround its external part. It is interesting that beautiful quartz crystals (with significant dimensions) come into sight in the gaps of the pegmatite body. Since the quartz is developed from the contacting fragments of the rock and feldspar, the dominant part of the quartz in Čanište is massive.

*Budinarci locality*

The Budinarci village is situated about 12 km northeast from the Berovo city. The rocks around the village are composed of micashists, gneisses and granites.

Quartz veins, which generically have pegmatite origin, intercept the gneisses very irregularly. The size of the veins varies and quartz appears as either well-formed crystal aggregates or beautiful monocrystal species, from transparent, across slightly smoky, to totally dull. Although quartz veins are dominant, the wide granite veins are also typical and found in the above mentioned rocks [34].

*Belutče locality*

The locality Belutče is situated on the southern part of Mariovo. Basically, it lies on a quartz-pegmatite vein that once has been used for the production of sodium feldspar (albite). The main minerals originating from this vein are apatite, orthoclase, microcline as well as quartz [35].

Here, it should be stressed that beautiful prismatic quartz monocrystals over 15 cm long from the pegmatite from Pelagon appear in the Belutče pegmatite body. These crystals are ideally developed and reach 15 cm in length. Although the transparent quartz samples are characteristic, the smoky quartz appears as well.

*Sasa locality*

The mineral composition of the ore mineralization in this locality is very complex and basically represented by a variety of minerals formed in different mineralization stages (metamorphic, scares, hydrothermal) [36, 37].

In the hydrothermal stage of formation of Sasa locality, an intensive silification represented with the small-grained quartz aggregate appears. The aggregate replaces the basic gneiss minerals. The appearance of considerable amounts of well-shaped crystalline quartz is characteristic as well as the common association of this mineral with galena, sphalerite and, occasionally, with the carbonate minerals.

*Zletovo locality*

In the lead-zinc vein type hydrothermal deposit, several major types of ore parageneses are established, particularly in the low temperature paragenesis where quartz and chalcedony minerals are included in the dominantly oxide-carbonate associations [38–40].

It should be emphasized that quartz appears in almost all phases of mineralization processes in Zletovo ore locality. Thus, quartz is present in high-temperature sulfide paragenesis together with pyrothine, marcasite, pyrite, sphalerite, chalcopyrite, galena, tetrahedrite, siderite and hematite. The presence of quartz is manifested in contact-metasomatic oxide paragenesis with magnetite, jacobsite, hausmanite, hematite, and garnet as well as in the mid-temperature sulfide-sulfosalts paragenesis. The association of quartz and chalcedony is basically present in low-temperature oxide-carbonate paragenesis where quartz appears accompanied with siderite, rhodochrosite, calcite and barite.

The formation of either crystal quartz aggregates or monocrystals in all the mentioned different temperature stages is typical.

*Češinovo locality*

The opalization is post-volcanic occurrence as a result of the influence of hydrothermal solution (rich in silicium) on the tuffs. In the series of the Kratovo-Zletovo volcanic area, especially in the locality Češinovo, the great content of volcanic tuffs occurs [41, 42]. The most dominant part of the hydrothermal changes is represented with the opal mineral form. The texture and different color varieties of opal occur as a consequence of the intensity of the process of hydrothermal metamorphosis on the tuffs. Some of them are characterized with the presence of tridymite on their surface.

*Mariovo locality*

Few pegmatite bodies appear in the gneisses of the Pelagon Metamorphic Complex known as a Mariovo locality. The bodies are built of the quartz and feldspar and, basically, have irregular shape and different size. Excluding the quartz and feldspar, the appearance of other pegmatite minerals like dystene, biotite, muscovite is usual. The quartz is released in the process of the surface decomposition and often found in the lower parts of the pegmatite bodies in the form of irregular and smaller or larger crystals [35]. Although the crystalline quartz is present, the massive forms of this mineral occur.

*Saždevo locality*

A gneiss-micashists series appears in the contact part of the Pelagonian-Metamorphic Complex and the West-Macedonian Zone near the Saždevo village. Here, quartz lenses appear, which sometimes, could reach 10 m in length. These lenses sometimes are additionally followed by the well-developed quartz crystals [33].

## RESULTS AND DISCUSSION

*Identification of quartz and opal by FT IR and Raman spectroscopy*

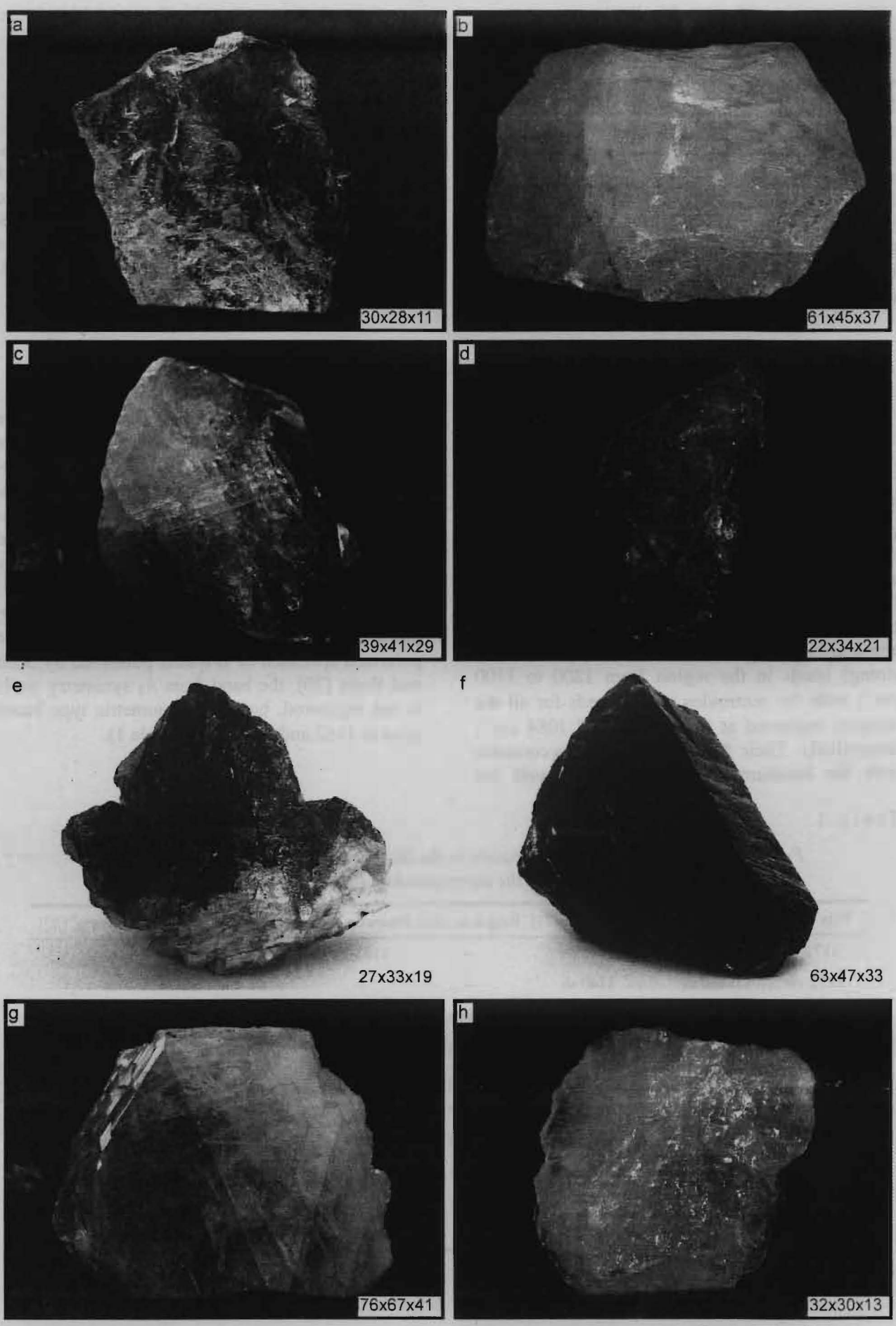
The infrared spectra of the studied samples of $\alpha$-quartz collected from Budinarci (Fig. 2, a-d) are presented in Fig. 3, a-d. As it can be seen, although the color of the samples significantly varies from almost transparent (Fig. 2, a) to almost opaque (Fig. 2, d) their spectra are identical. The most expressed feature in the spectra of the samples is the appearance of triplet of (medium, very weak and strong) bands in the region from 1200 to 1100 $cm^{-1}$, with the centroides of the bands for all the samples registered at 1172, 1152 and 1084 $cm^{-1}$, respectively. Their frequencies are in accordance with the literature data, where these bands are found at 1172, 1150 and 1084 $cm^{-1}$ by Moenke [22] and at 1165, 1140 and 1085 $cm^{-1}$ by Taylor et al. [21] (Table 1). The first and the last mode belong to $E$, whereas the remaining one to $A_2$ symmetric type [22]. In the same spectral region, Patersson [24] registered only two bands at 1163 and 1084 $cm^{-1}$. On the other hand, in the infrared spectra of powdered quartz sample from Plyusnina [23] and Reig et al. [25], only one intensive band appears at 1098 and 1088 $cm^{-1}$, respectively. In the polarized spectrum of $\alpha$-quartz published by Scott and Porto [20], the band from $A_2$ symmetry mode is not registered, but the $E$ symmetric type bands arise at 1162 and 1072 $cm^{-1}$ (Table 1).

Table 1

*Frequencies and intensities of the bands in the IR spectra of powdered quartz samples compared with the corresponding literature data*

| This work[a] | Moenke [22] | Taylor et al. [21] | Reig et al. [25] | Patersson [24] | Plyusnina [23] | Scott and Porto[b] [20] |
|---|---|---|---|---|---|---|
| 1172 w | 1172 sh | 1165 sh | – | 1163 sh | – | 1162 w |
| 1152 vw | 1150 sh | 1140 sh | – | – | – | – |
| 1084 s | 1084 s | 1085 s | 1088 s | 1084 s | 1098 vs | 1072 w |
| 798 m | 798 m | 798 m | 798 m | 799 m | 804 m | 807 m |
| 779 m | 780 m | 779 m | 779 m | 782 m | – | 795 m |
| 695 w | 697 w | 694 w | 694 w | | 695 w | 697 w |
| 514 sh | 512 sh | 512 w | 515 sh | | – | 509 m |
| 461 s | 462 s | 460 s | 467 s | | 468 s | 450 s |
| 397 w | 398 w | 397 w | | | | 394 w |
| 373 w | 373 w | 370 w | | | | – |

[a]All bands appear at identical frequencies.
[b]Transverse modes.

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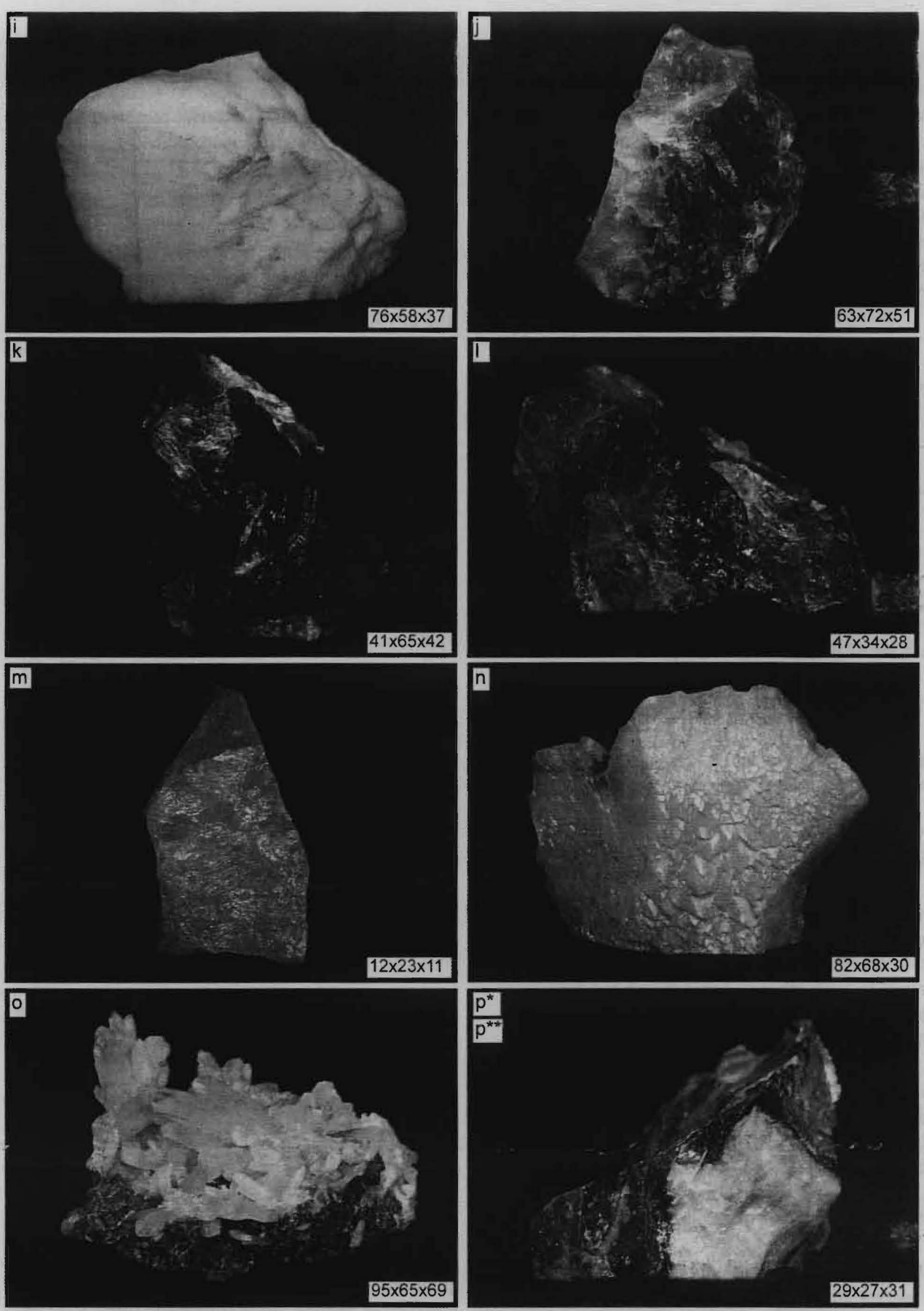


Fig. 2. The quartz samples from Budinarci, a - d, Alinci (e - smoky), (f - morion), Belutce (g), Mariovo (h, i), Mariovo-gray and transparent (j - light, k - dark), Canište (l), Sasa (m), Sa•devo (n), Zletovo (o) and yellow (p*) and red (p**) opal from Cešinovo

Going towards lower frequencies, the doublet at 798 and 779 $cm^{-1}$ is observed in all the infrared spectra of the studied Budinarci samples (Fig. 3). According to Plyusnina [23], the first band could be blue shifted up to 804 $cm^{-1}$, whereas the appearance of the second one is tolerated in the 779–782 $cm^{-1}$ region [21–25]. Their appearance is registered at 807 (longitudinal) and 795 $cm^{-1}$ (transverse vibration) in the polarized spectra of quartz [20].

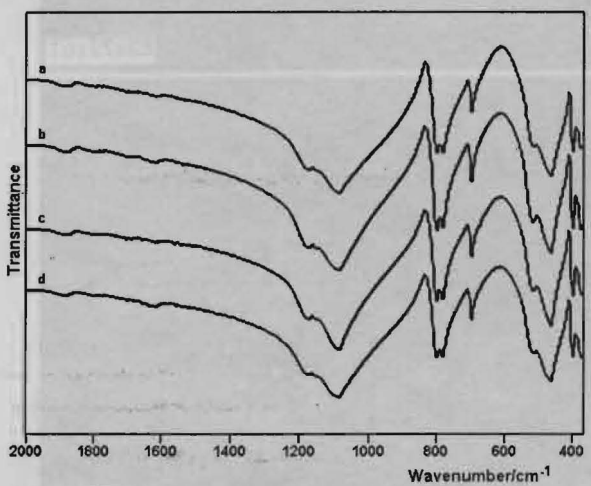


**Fig. 3.** The FT IR spectra of quartz samples from Budinarci, a-d

The bands below 700 $cm^{-1}$ in the spectra of the samples from Budinarci (Fig. 3, a-d) also appear at the same frequencies, being again in accordance with the published powder IR spectra (Table 1). It is another striking evidence for the preliminary identification of these samples as quartz minerals.

The infrared spectra of the remaining studied samples of $\alpha$-quartz (Fig. 2, e-o) collected from other localities from Macedonia are presented in Fig. 4, a-k. There is no doubt that the spectra are identical to each other and that their band frequencies are nearly the same as those from the samples from Budinarci (Fig. 3).

Since all infrared spectra are identical, it is obvious that IR spectroscopy could not discriminate between the different colored quartz samples and connect the color with some spectral characteristics and vice versa. In other words, it is impossible, only by the infrared spectrum of the quartz sample to recognize its color.

The relevant conclusion about the color of the opal samples is also impossible if only their infrared spectra are compared. Although the two studied samples have different color (yellow and red, Fig. 2, p* and p**, respectively), their infrared spectra (Fig. 4, l* and l**, respectively), as in the case of quartz, are indistinguishable from each other. Namely, three bands are observed in the opal spectra in the 1200–400 $cm^{-1}$ region. The most typical opal IR band is the strongest, complex, but not well defined maximum at 1103 $cm^{-1}$. The frequency of this band in the literature is obtained between 1098 [23] and 1102 $cm^{-1}$ [22]. The remaining two bands observed at 792 and 474 $cm^{-1}$ (Fig. 4, l* and l**), are also in consistence with the literature data, registered at 804 and 468 $cm^{-1}$ [23] and at 790 and 490 $cm^{-1}$ [22]. In the spectrum published by Moenke [22], additional shoulder on the higher frequency side of the lowest frequency band is detected at 503 $cm^{-1}$, whereas in our spectra its occurrence is not well developed.

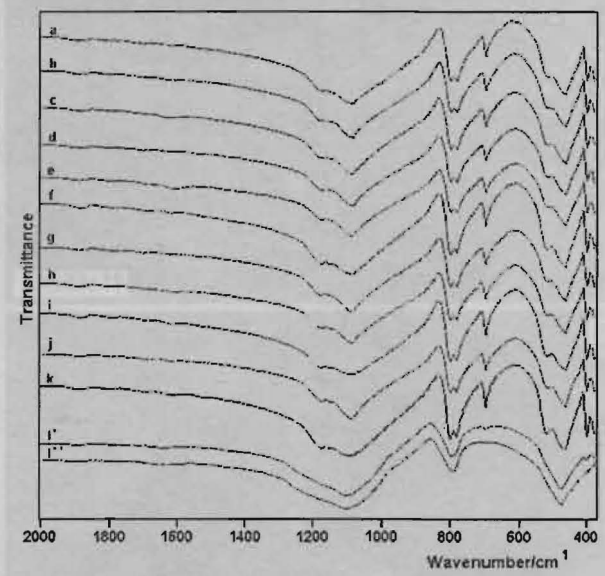


**Fig. 4.** The FT IR spectra of quartz samples from Alinci (a – smoky), (b – morion), Belutče (c), Mariovo (d, e), Mariovo – gray and transparent (f – light, g – dark), Čanište (h), Sasa (i), Saždevo (j), Zletovo (k) and yellow (l*) and red (l**) opal from Češinovo

The study continued by recording the Raman spectra of the quartz samples from Budinarci (Fig. 5, a-d) in order to see whether this technique can discriminate between differently colored quartz samples (Fig. 2, a-d). As seen from the spectra, the same number of bands in the spectral region below 1200 $cm^{-1}$ is observed. Furthermore, the frequencies of these nine bands are almost identical to each other and are very similar with the corresponding literature data [27–30]. In order to compare them with the literature data, the band frequencies for the Raman spectrum of the most transparent sample from Budinarci (Fig. 2, a) are given in Table 2.

Table 2

*Frequencies and intensities of the bands below 1200 cm$^{-1}$ in the Raman spectrum of powdered quartz sample from Budinarci (Fig. 5a) compared with the corresponding literature data*

| This work[a] | Burgio and Clark [30] | McMillan [27] | McMillan et al. [28] | Wang et al.[b] [29] |
|---|---|---|---|---|
| – | – | – | 1229 vw | – |
| 1158 vw | 1160[b] vw | 1160[b] vw | 1159 vw | 1160 vw |
| 1070 vw | 1070[b] vw | 1060[b] vw | 1082 vw | – |
| 797 vw | 800[b] vw | 800[b] vw | 808 vw | 790 vw |
| 694 vw | 695[b] vw | 690[b] vw | 696 vw | 690 vw |
| 462 s | 466 s | 464 s | 510 vw | 465 s |
| 396 w | 398 vw | 395[b] vw | 395 vw | 390 w |
| 353 w | 354 vw | 354 w | 354 w | 360 w |
| 260 w | 262 vw | 263[b] vw | 264 vw | 260 vw |
| 200 m | 208 m | 206 m | 206 m | 210 m |
| | 130 m | 128 m | 128 m | 130 m |

[a] All bands appear at almost identical frequencies.
[b] The frequencies are approximate because they are not numerically given.

Only minor differences in the relative intensities between some of the peaks are observed. The frequency variations are entirely due to the different sample orientation in the Raman experiment [43].

Although the spectra in this region are almost identical to each other, significant difference in the number of the bands and especially in the intensities of the bands above 1200 cm$^{-1}$ is observed (Fig. 5, a-d). Namely, in the spectra of the most opaque samples from Budinarci (Fig. 2, c-d), a doublet of bands appears at 1404 and 1374 cm$^{-1}$, whereas in the spectra of the most transparent samples (Fig. 2, a-b) the unique band at 1392 cm$^{-1}$ is registered (Fig. 5, a-d). Additional bands are observed at around 1510, 1790 and 1940 cm$^{-1}$ in the samples (Fig. 5, b-d). Their intensity is again superior for the both dimmed samples (Fig. 2, c-d). Since no bands are expected to appear above 1229 cm$^{-1}$ according to the literature Raman data [28], their registration is surprising. Most probably the bands above 1200 cm$^{-1}$ are due to the sample impurities.

The Raman spectra of other studied quartz samples from Macedonia (presented in Fig. 2, e-o), are very similar in 1200–150 cm$^{-1}$ region (Fig. 6, a-k). Slightly expressed differences are observed above this region, in the terms of appearance of weak bands, particularly present in the spectra of the samples from Mariovo.

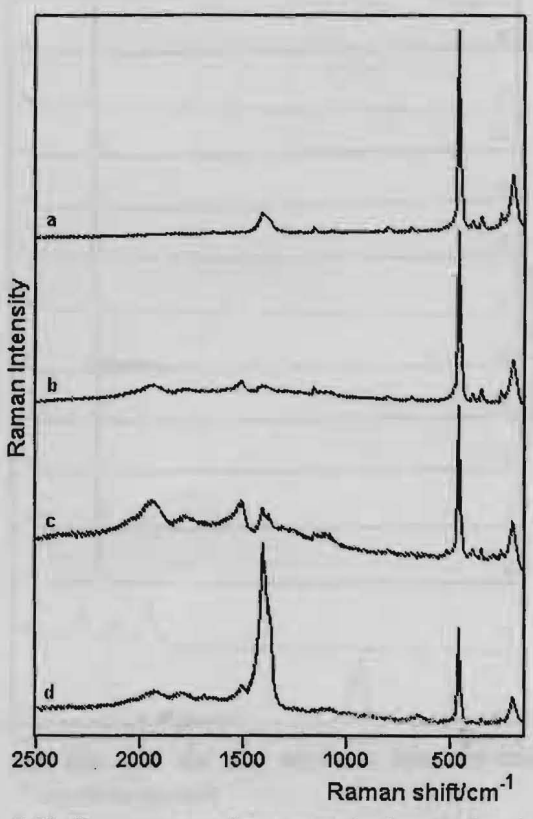


**Fig. 5.** The Raman spectra of quartz samples from Budinarci, a–d

The Raman spectra of the yellow and red opal samples presented in Fig. 6, l* and l**, respectively, are significantly different. The spectrum of red

opal is not adequate to the Raman spectrum of opal known from the literature. Probably the incident laser beam burns the sample. Therefore, this spectrum can not be compared with its yellow analogue and can not serve for opal identification purposes. However, the Raman spectrum of the yellow sample is in agreement with the corresponding literature data [44]. According to the Ostrooumov [44], the position of the lowest frequency Raman band can be used to classify the degree of crystallinity of opals. In other words, the band wavenumber for best crystallized opals is around 325 $cm^{-1}$ approaching to 400 $cm^{-1}$ for the most amorphous specimen [44]. Thus, the appearance of this band in our spectrum at 393 $cm^{-1}$ (Fig. 6, l*) serves as an evidence that yellow opal is amorphous and does not possess any degree of crystallinity. Obviously, the Raman bands seem to be more characteristic for the geographical as well as geological origin (volcanic or sedimentary) of the sample, rather than being a powerful tool for correlation of the opal color vs. its chemical composition.

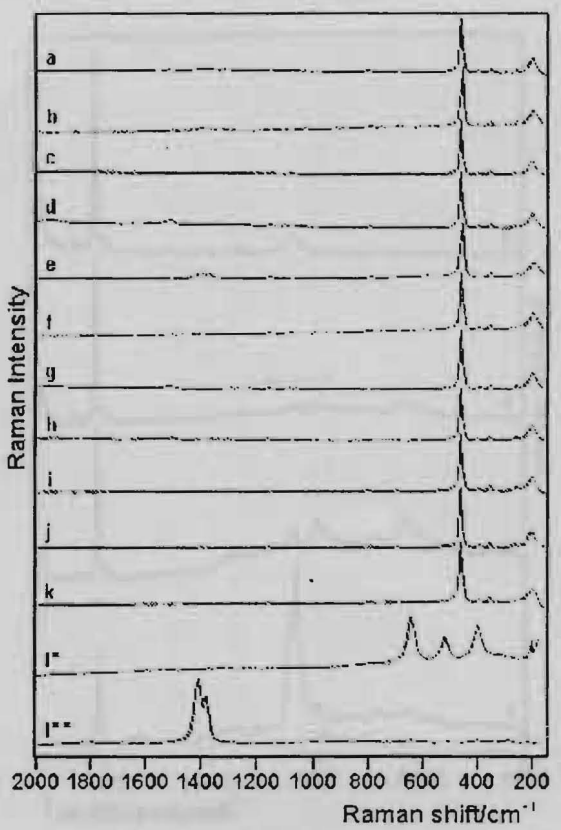


**Fig. 6.** The Raman spectra of quartz from Alinci (a – smoky), (b – morion), Belutče (c), Mariovo (d, e), Mariovo – gray and transparent (f – light, g – dark), Čanište (h), Sasa (i), Saždevo (j), Zletovo (k) and yellow (l*) and red (l**) opal from Češinovo

*Chemical analysis of the studied quartz and opal samples*

One of the major problems in ETAAS is matrix interferences. Therefore, the interference of Si (as a matrix element in the quartz and opal) on the investigated elements is studied. It is shown that Si tends to decrease absorbance of the most of the elements and therefore the method for elimination of silicium (using HF) is proposed. Optimal instrumental parameters for AAS determination are established by extensive testing for each investigated element. Depending on concentration levels of the investigated element, two different atomizers are used: flame (for Al, Ca, Fe, Mg, Mn and Zn) and graphite furnace (for Cd, Co, Cr, Cu, Ni and Pb). Sodium and potassium are analyzed by flame emission spectrometry.

Results from the determination of investigated elements in quartz and opal samples taken from different localities in the Republic of Macedonia are given in Tables 3 and 4.

As it can be seen, the content of Ca in quartz samples from Budinarci (a and d), Saždevo, Sasa and Zletovo, is significantly higher than in the other studied quartz minerals. The comparison of the color of these samples with the color of other specimens undoubtly shows that higher content of Ca leads to milky colored samples. In some cases, according to Mottana et al. [1] milky quartz appears white due to numerous bubbles of gas and liquid in the crystal.

As it is suggested by Rossman [2], the light or dark brown to black color is due to Al content in the quartz minerals. Smoky quartz, on the other hand, is associated with substitutional Al, with concentration ranging up to a few thousand ppm. In fact, the smoky quartz color is due to the presence of an oxygen ion, $O^-$ (with a single unpaired electron) bound to a substitutional Al ion [2]. In our investigation it is found (Table 3) that the quartz samples from Budinarci (c and d), and the morion from Alinci are smoky dimmed and have the highest content of Al (0,525–3,623 %). Also, the higher content of Pb and Mn in these samples can point out those inclusions of those two elements which give additional contribution to the dark color of the samples.

It is suggested in the literature that green color of quartz is directly related to its Ni content [1, 8] and that even traces of Ni introduce green variety in quartz minerals [45].

Table 3

*The content of some trace elements (given as oxides) in natural quartz and opal samples from Macedonia (in %)*

| Locality and figure | $w(Na_2O)$ | $w(K_2O)$ | $w(CaO)$ | $w(MgO)$ | $w(PbO)$ | $w(Fe_2O_3)$ | $w(MnO)$ | $w(Cr_2O_3)$ | $w(Al_2O_3)$ | $w(ZnO)$ | $w(CuO)$ | $w$(oxides) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Budinarci (Fig 2. a) | 0.591 | 0.182 | 0.972 | 0.296 | 0.156 | 1.264 | 0.177 | 0.001 | 0.204 | 0.005 | 0.002 | 3.850 |
| Budinarci (Fig 2, b) | 0.074 | 0.008 | 0.294 | 0.308 | 0.213 | 2.248 | 0.258 | 0.015 | 0.305 | 0.013 | 0.014 | 3.750 |
| Budinarci (Fig 2, c) | 0.507 | 0.003 | 0.425 | 0.316 | 0.248 | 1.959 | 0.265 | 0.016 | 0.525 | 0.020 | 0.008 | 4.292 |
| Budinarci (Fig 2, d) | 0.126 | 0.033 | 0.757 | 0.072 | 0.323 | 1.962 | 0.501 | 0.030 | 0.743 | 0.014 | 0.004 | 4.565 |
| Alinci (Fig. 2, e) | 0.216 | 0.003 | 0.172 | 0.046 | 0.359 | 4.052 | 0.654 | 0.041 | 0.326 | 0.017 | 0.020 | 5.806 |
| Alinci (Fig. 2, f) | 0.039 | 0.013 | 0.689 | 0.158 | 0.251 | 3.844 | 0.323 | 0.029 | 2.633 | 0.077 | 0.012 | 8.068 |
| Belutče (Fig. 2, g) | 0.050 | 0.013 | 0.728 | 0.338 | 0.167 | 0.287 | 0.249 | 0.014 | 0.461 | 0.016 | 0.002 | 2.325 |
| Mariovo (Fig. 2, h) | 0.055 | 0.003 | 0.255 | 0.223 | 0.107 | 0.275 | 0.127 | 0.015 | 0.266 | 0.004 | 0.002 | 1.332 |
| Mariovo (Fig. 2, i) | 0.033 | 0.001 | 0.226 | 0.203 | 0.114 | 0.160 | 0.122 | 0.017 | 0.152 | 0.002 | 0.002 | 1.032 |
| Mariovo (Fig. 2, j) | 0.077 | 0.009 | 0.369 | 0.310 | 0.002 | 2.102 | 0.266 | 0.036 | 0.023 | 0.009 | 0.010 | 3.213 |
| Mariovo (Fig. 2, k) | 0.022 | 0.002 | 0.439 | 0.317 | 0.203 | 1.068 | 0.223 | 0.027 | 0.029 | 0.004 | 0.003 | 2.337 |
| Čanište (Fig. 2, l) | 0.037 | 0.001 | 0.391 | 0.300 | 0.210 | 1.050 | 0.185 | 0.023 | 0.094 | 0.006 | 0.003 | 2.300 |
| Sasa (Fig. 2, m) | 1.349 | 0.002 | 0.850 | 0.276 | 0.002 | 2.572 | 0.189 | 0.037 | 0.232 | 0.005 | 0.003 | 5.517 |
| Saždevo (Fig. 2, n) | 0.205 | 0.019 | 0.866 | 0.276 | 0.132 | 1.226 | 0.156 | 0.013 | 0.376 | 0.006 | 0.002 | 3.277 |
| Zletovo (Fig. 2, o) | 0.031 | 0.003 | 0.806 | 0.293 | 0.010 | 1.727 | 0.189 | 0.009 | 0.190 | 0.008 | 0.014 | 3.280 |
| Češinovo (Fig. 2, p*) | 0.257 | 0.201 | 1.254 | 0.117 | 0.131 | 3.168 | 1.147 | 0.096 | 3.262 | 0.015 | 0.013 | 9.661 |
| Češinovo (Fig. 2, p**) | 0.062 | 0.047 | 0.347 | 0.328 | 0.115 | 10.502 | 0.435 | 0.049 | 1.783 | 0.014 | 0.004 | 13.689 |

On the other hand, Rossman [2] states that the green color arises from admixed fine-grained nickel compounds in the silica matrix rather than from substitutional Ni in the silica itself. However, Vasconcelos et al. [45] suggested that Rossman's hypotheses should be revised because they found that blue-green color of mineral chrysoprase is associated with the presence of nanoinclusions of a nickel phyllosilicate, tentatively identified as the Ni-talc, willemseite. The presence of Ni which is responsible for the green color, is in accordance with the results of our investigation, where the highest content of Ni amounting from 6.67 to 18.19 μg/g is found in the samples from Budinarci – d, Belutče and both samples from Alinci.

The presence of iron oxides is responsible for the red markings of quartz. Namely, various mineral pigments (hematite, goethite, limonite) contribute to red color [1, 2, 18], this color being the most common for opal minerals. The red hues observed in the opal samples are commonly associated with +3 oxidation state of iron [2]. Our study confirmed the higher content of Fe obtained in the quartz sample from Budinarci-b, smoky quartz and morion sample from Alinci as well as in the opal samples (especially in the red variety) which is another striking evidence for the red color in these minerals.

Table 4

*The content of traces of Cd, Co and Ni (given as oxides) in natural quartz and opal samples from Macedonia (in μg/g)*

| Locality and figure | CdO | CoO | NiO |
|---|---|---|---|
| Budinarci (Fig 2, a) | 0.089 | 0.663 | 6.222 |
| arci (Fig 2, b) | 0.064 | 2.399 | 6.223 |
| Budinarci (Fig 2, c) | 0.066 | 0.835 | 6.674 |
| Budinarci (Fig 2. d) | 0.058 | 2.105 | 11.79 |
| Alinci (Fig. 2, e) | 0.027 | 2.481 | 11.33 |
| Alinci (Fig. 2, f) | 2.615 | 0.036 | 18.19 |
| Belutče (Fig. 2, g) | 1.882 | 0.025 | 7.407 |
| Mariovo (Fig. 2, h) | 1.287 | 0.014 | 2.713 |
| Mariovo (Fig. 2, i) | 1.299 | 0.017 | 1.897 |
| Mariovo (Fig. 2, j) | 0.007 | 1.504 | 9.192 |
| Mariovo (Fig. 2, k) | 0.009 | 0.967 | 4.964 |
| Čanište (Fig. 2, l) | 0.794 | 0.022 | 5.336 |
| Sasa (Fig. 2, m) | 1.843 | 0.022 | 5.993 |
| Saždevo (Fig. 2, n) | 1.321 | 0.008 | 4.437 |
| Zletovo (Fig. 2, o) | 1.846 | 0.126 | 12.68 |
| Češinovo (Fig. 2, p*) | 1.413 | 0.035 | 10.81 |
| Češinovo (Fig. 2, p**) | 2.138 | 0.053 | 5.945 |

## CONCLUSIONS

It is presented that vibrational (infrared and Raman) spectroscopy could not discriminate between the different color varieties of quartz and opal as well. However, the mentioned minerals from Macedonia have not been previously systematically studied by vibrational spectroscopy, the presented spectral data being significant contribution in their identification and characterization.

The performed complete chemical analysis shows that the trace element content is the only reason for different colors of these quartz samples. Thus, the red color of quartz and opal is connected with the presence of Fe, the green varieties have significant amount of Ni, Ca leads to milky colored samples, and light or dark brown to black color is due to the present Al, Pb and Mn trace element(s).

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Резиме

## МИНЕРАЛИ ОД МАКЕДОНИЈА
## XII. ВЛИЈАНИЕ НА СОДРЖИНАТА НА ЕЛЕМЕНТИТЕ ВО ТРАГИ ВРЗ БОЈАТА НА КВАРЦ И ОПАЛ – ААС, ФТ-ИЦ И МИКРО-РАМАНСКИ СПЕКТРОСКОПСКИ ИЗУЧУВАЊА

**Петре Макрески[1], Глигор Јовановски[1], Трајче Стафилов[1], Блажо Боев[2]**

*[1]Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј", п. фах 162, МК-1001 Скопје, Република Македонија*
*[2] Завод за петрологија, минералогија и геохемија, Рударско-геолошки факултет, Универзитет „Св. Кирил и Методиј", Гоце Делчев 89, МК-2000 Штип, Република Македонија*
petremak@iunona.pmf.ukim.edu.mk

**Клучни зборови:** кварц; опал; боја; минерали; Македонија; ФТ-ИЦ спектроскопија; раманска спектроскопија; атомска апсорпциона спектрометрија

Изучувана е зависноста на бојата на природните минерали кварц и опал собрани од различни локалитети во Република Македонија (Алинци, Белутче, Будинарци, Мариово, Саса, Саждево, Чаниште, Чешиново, Злетово) од содржината на елементите во траги со примена на Фуриеовата трансформна инфрацрвена спектроскопија (ФТ-ИЦ), микрораманска спектроскопија и атомска апсорпциона спектрометрија (ААС). За определување на содржината на различни елементи во траги (Al, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb и Zn) испитувани се 15 примероци од кварц и 2 примерока од опал со користење на пламената атомска апсорпциона спектрометрија (ПААС) и Земановата електротермичка атомска апсорпциона спектрометрија (ЕТААС). За елиминирање на влијанието на матрицата предложен е метод за отстранување на силициумот. Утврдени се оптималните инструментални услови за определување на секој испитуван елемент со

примена на ETAAC (температура и време на сушење, пиролиза и атомизација). Најдено е дека млечно белата боја на примероните од кварц се должи на присуството на траги од Ca, појавата на црно обојување е како резултат на присуство на нечистотии од Pb, Mn и Al, а присуството на Fe и Cr доведува до појава на црвено, односно зелено обојување на минералните примероци.

Идентификацијата на минералите е извршена со споредба на добиените резултати од инфрацрвената и раманската вибрациона спектроскопија со соодветните литературни податоци добиени за испитуваните примероци на минерали.

Даден е преглед на основните морфолошки и физичко-хемиски карактеристики на минералите кварц и опал, како и геологијата на локалитетите од кои се земени минералите. Прикажани се и слики во боја од сите изучувани примероци.